



# Catalytic formation of 2,3,3,3-tetrafluoropropene from 2-chloro-3,3,3-trifluoropropene at fluorinated chromia: A study of reaction pathways



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## ABSTRACT

The catalytic gas phase reaction between  $\text{CF}_3\text{—CCl=CH}_2$  with HF yielding  $\text{CF}_3\text{—CF=CH}_2$  was investigated regarding the reaction pathways involved. Different from the reaction under liquid phase (homogenous) conditions, in heterogeneous phase  $\text{CF}_3\text{—CCl=CH}_2$  does not add HF forming the saturated intermediate  $\text{CF}_3\text{—CFCl—CH}_3$  but undergoes direct Cl/F exchange at the starting olefin molecule resulting directly in the formation of  $\text{CF}_3\text{—CF=CH}_2$ . This might be caused mainly by the fact that under heterogeneous gas phase conditions higher temperatures are needed as compared to liquid phase conditions thus suppressing the formation of kinetically less stable  $\text{CF}_3\text{—CFCl—CH}_3$  under these conditions. Since for all the reaction steps involved in this complex reaction system the Gibbs free reaction enthalpy values are close to zero [1], the selectivity towards several reaction products is strongly dependent on the reaction parameters, e.g. temperature, pressure and molar ratio of the reactants. Based on the catalytic data obtained for fluorinated chromia as catalyst, a reaction path distinguishing direct chlorine against fluorine exchange versus hydrofluorination/dehydrochlorination is proposed.

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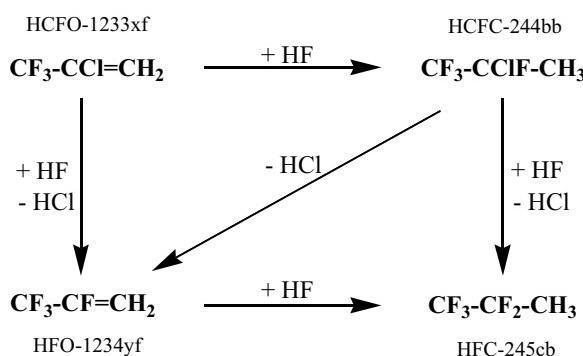
## 1. Introduction

Haloalkenes are very important starting compounds for halogen containing polymers (e.g. PVC, PVdC, PVDF, PTFE). Moreover, the global warming potential (GWP) of 1,1,1,2-tetrafluoroethane (HFC-134a) has caused an intense search for lower GWP alternatives. This prompted the European Community to stop its use as a refrigeration agent for air conditioning devices, e.g. in automobiles.

Hydrofluorolefins (HFOs) have been considered as favourable replacements for saturated hydrofluorocarbons (HFCs) due to their zero ozone depletion potential (ODP) and a very low GWP respectively [2,3]. Moreover, HFOs exhibit very low toxicity and flammability [4–6] and as a result, 2,3,3,3-tetrafluoropropene,  $\text{CF}_3\text{—CF=CH}_2$ , (HFO-1234yf) has been identified as a promising compound to be used as a replacement as indicated by Wallington et al. and Luecken et al. [7,8].

Several reaction pathways might be designed to end up with the targeted product HFO-1234yf. A straightforward reaction sequence to the desired HFO-1234yf is fluorination of the hydrochlorofluoroolefin (HCFO) 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) with HF in the presence of a suitable fluorination catalyst as presented by Eq. (1). However, this is an overly simplified reaction path which does not at all reflect the real reactions that might take place depending on the catalyst and the catalytic conditions established. As can be predicted from Scheme 1, the real reaction system is much more complicated and might even be more complex when isomers of the several possible intermediates are taken into account. The most open issue is to identify the reaction pathway that could lead to HFO-1234yf from HCFO-1233xf. This can proceed either via direct fluorine replacement of the chlorine atom on the HCFO-1233xf molecule as represented by Eq. (1) or via the saturated intermediate 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb). In other words, the main question is whether or not the reaction of HCFO-1233xf with HF to HFO-1234yf proceeds via HF addition (with HCFC-244bb as intermediate) followed by loss of HCl, or through direct chlorine/fluorine exchange reaction. It is generally accepted that direct F-for-Cl replacement at an olefinic

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**Scheme 1.** Possible reaction pathways for the reaction of HCFO-1233xf with HF.

C atom is not favourable whereas this is very likely for an  $sp^3$  C atom. Hence, the intermediate formation of the saturated HCFC-244bb as intermediate as it is evidenced in case of the catalytic liquid phase reaction had to be considered for the heterogeneous reaction too. Unfortunately, there is no academic publication on the mechanism of this new but industrially important reaction, just two articles appeared very recently focusing on the characterization of the fluorinated chromia catalyst employed [9,10]. Therein the authors emphasize how synthesis conditions of the fluorinated chromia based catalyst influences the catalytic performance from HCFO-1233xf to HFO-1234yf. The most surprising outcome was that a pre-calcination temperature of about 550 °C causing a crystallization of the catalyst resulted in the best catalytic performance of 63.3% conversion with 59% selectivity for HFO-1234yf and 38% for HFC-245cb. Moreover, carbon deposit at the surface was found to be the major reason for slow deactivation of the catalyst. Thus, the reactivation of the chromia catalyst by oxygen treatment as reported in [10] is logic and in line with many earlier reports on reactivation of chromia based fluorination catalysts (see [11] and references therein). However, information regarding the mechanism/reaction path has not been given. Just from patent literature information regarding the reaction path under catalytic liquid phase conditions is accessible even though this is very limited. Thus, starting from HCFO-1233xf, two different reaction paths have to be taken into account (cf. Scheme 1): (i) preliminary formation of HCFC-244bb followed by further formation of either HFO-1234yf or HFC-245cb and (ii) direct formation of HFO-1234yf which may undergo further consecutive reaction thus forming HFC-245cb. According to the patent literature, it is possible to run a two-step process in which the second step (reaction of HCFO-1233xf) is performed under liquid phase homogeneous catalytic conditions in the presence of antimony pentachloride based catalysts whereupon HFO-1234yf is formed via formation of HCFC-244bb as intermediate [12]. An alternative gas phase process for both reaction steps (formation of HCFO-1233xf and HFO-1234yf) using fluorinated chromia as the heterogeneous catalyst was recently proposed [10]. Unfortunately but expectedly, no information is given regarding the reaction pathway, thus no further input for the work intended in this article could be extracted.

Since the knowledge of the reaction path and the formation of the different possible intermediate compounds are closely related to the dependency of each single reaction step from the reaction conditions, the fundamental understanding of the reaction path is a mandatory basis to control and optimize the reaction conditions. Hence, the present work was intended to elucidate the reaction path of the formation of HFO-1234yf starting from HCFO-1233xf under heterogeneous catalytic gas phase conditions employing a fluorinated chromia catalyst. Therefore, less attention was laid on the optimization of the chromia catalysts since one of us has long time experience with this kind of fluorination catalysts [11].

Therefore a fluorinated chromia catalyst which has shown optimal conditions in the fluorination of C2-haloalkanes was chosen as a standard catalyst. Instead, the main focus was laid on investigating the reactivity and halogen exchange behavior of each possible single intermediate compound by varying the reaction conditions in order to get deeper insights into the mechanism/reaction path of the reactions according to Scheme 1. Fluorinated chromia is by far the most commonly used and most frequently investigated catalyst for this kind of chlorine/fluorine exchange reaction [11,13–16] therefore similar chromia phases were likely to be used for these investigations. Since the main characteristics of these kinds of catalysts have been extensively published many years ago and even the cited publications [9,10] did not add fundamentally new insights, we pretend to repeat these data, and therefore, will just briefly give the details of catalyst preparation and treatment.

## 2. Experimental

### 2.1. Catalyst preparation

The fluorinated chromia catalyst (designated as F-Cr<sub>2</sub>O<sub>3</sub>) was prepared by fluorination of freshly prepared chromia (~5 g) with 20 ml min<sup>-1</sup> gaseous HF (Solvay Fluor GmbH) at 350 °C for 16 h in a flow-thru system (Fluorine content 30–40%, determined by fluoride sensitive electrode after soda-potash fusion). To obtain freshly precipitated chromium hydroxide Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Sigma-Aldrich, 99%) was first dissolved in water (0.4 M) followed by addition of ammonia (Acros Organics, 28–30 wt%) until pH = 8 was reached. The precipitated solid was separated, washed three times with deionised water and finally calcined at 400 °C for 5 h (previous heating rate 1 °C/min).

The HS-AlF<sub>3</sub> catalyst (HS = high surface area) was prepared according the fluorolytic sol gel synthesis as described in [17]. In brief, aluminium isopropoxide (Sigma-Aldrich, 98%) was dissolved in isopropanol (Sigma-Aldrich, 98%, dried with standard method) and then a stoichiometric amount anhydrous HF (Solvay Fluor GmbH) dissolved in isopropanol was added. After stirring overnight, the solvent was removed under reduced pressure and elevated temperature (80 °C in maximum). The dried AlF<sub>3</sub>-xerogel was directly used and activated under *in situ*-conditions with chlorodifluoromethane (Solvay Fluor GmbH).

Barium and strontium chloride fluoride catalysts (designated BaClF and SrClF) were prepared by *in-situ* chlorination during reaction with HFC-244bb from respective fluorides (Sigma-Aldrich, 99.99%) as shown in [18].

### 2.2. Catalytic reactions

An Inconel tube with a stopper of silver wool was used as steady flow reactor. The organic chlorofluorocarbon compounds (supplied by SynQuest Laboratories: 2-chloro-3,3,3-trifluoropropene (98%), 2,3,3,3-tetrafluoropropene (97%), 2-chloro-1,1,1,2-tetrafluoropropane (98%) and 1,1,1,2,2-pentafluoropropane (99%)) and carrier gases (air and argon) were dosed via mass flow controllers (Quantum Series from Brooks Instruments). HF (Solvay Fluor GmbH) was dosed using a Sonic Nozzle or with a customized mass flow controller from Millipore. The reaction gas mixture leaving the reactor was passed through a sodium hydroxide solution to trap acid gases followed by a calcium chloride column for drying purposes. The detailed reaction conditions for each performed experiment are listed in Table 1. The analysis of the reaction mixtures was performed by gas chromatography either with a Shimadzu GC 17A or Agilent Technologies 7890 gas chromatograph equipped with a GS-GASPRO or ShinCarbon column.

**Table 1**

Reaction conditions for performed catalytic reactions.

Figure, table or chapter	Catalyst	Temperature	Pressure	Contact time	HF: Educt: Air: Ar	GC
Fig. 1, Fig. 2	F-Cr <sub>2</sub> O <sub>3</sub>	350 °C	1 bar	20 s	20:1:0.2:0	TCD
Fig. 3	F-Cr <sub>2</sub> O <sub>3</sub>	250–350 °C	1 bar	25 s	4:1:0: 2	FID <sup>b</sup>
Table 3	F-Cr <sub>2</sub> O <sub>3</sub>	350 °C	1 bar	20 s	20:1:0.2:0	TCD
Table 3	F-Cr <sub>2</sub> O <sub>3</sub>	350 °C	3–7 bar	20 s	20:1:1:0	TCD
Fig. 4	F-Cr <sub>2</sub> O <sub>3</sub>	350 °C	1 bar	0.1–10.0 s	10:1:1.3:0	FID <sup>b</sup>
Fig. 5	F-Cr <sub>2</sub> O <sub>3</sub>	250–350 °C	1 bar	25 s	4:1:0:2	FID <sup>b</sup>
Section 3.2.2	F-Cr <sub>2</sub> O <sub>3</sub>	350 °C	1 bar	20–60 s	1–40 <sup>a</sup> :1:0:0–2	TCD
Fig. 6	F-Cr <sub>2</sub> O <sub>3</sub>	250–350 °C	1 bar	25 s	0:1:0:2	FID <sup>b</sup>
Table 4	F-Cr <sub>2</sub> O <sub>3</sub>	350 °C	2 bar	20 s	10:1:0.4:0	TCD
Table 4	HS-AlF <sub>3</sub>	350 °C	2 bar	40 s	10:1:0.4:0	TCD
Table 4	SrClF	350 °C	2 bar	40 s	10:1:0.4:0	TCD
Table 4	BaClF	350 °C	2 bar	40 s	10:1:0.4:0	TCD
Fig. 7, Table 5	F-Cr <sub>2</sub> O <sub>3</sub>	350 °C	1 bar	0.1–4.8 s	0:1:1:4	TCD

<sup>a</sup> HCl instead of HF.<sup>b</sup> No detection of CO<sub>x</sub>, molar ratios are given for gas-phase composition in column 3.

### 2.3. Catalyst characterization

X-ray powder diffraction measurements were performed using a Seifert XRD 3003 TT diffractometer using CuK<sub>α</sub> radiation. Moisture sensitive samples were prepared in a glove box and covered with a Kapton-foil. The solids used for catalysis were identified based on the ICSD powder diffraction file [19].

Surface area measurements were performed on a Micromeritics ASAP 2020 at 77 K by nitrogen adsorption. Before the measurement, the solids were degassed at 120 °C and 5 × 10<sup>-5</sup> mbar for twelve hours. Isotherms were processed by the Brunauer–Emmett–Teller method (BET).

## 3. Results

### 3.1. The catalytically active phases

#### 3.1.1. XRD patterns

The XRD patterns of fluorinated chromia (F-Cr<sub>2</sub>O<sub>3</sub>) (Fig. S1 in SI) indicated no crystalline phases. No reflections of Cr<sub>2</sub>O<sub>3</sub> or CrF<sub>3</sub> were obtained although the F-content ranged between 30 and 40%. This finding is in agreement with former reports [20] where possibly formed Cr<sub>3-x</sub>O<sub>x/2</sub>- and/or CrF<sub>3</sub>-phases appear X-ray amorphous. HS-AlF<sub>3</sub> is known to be X-ray amorphous [17] and that is the case here too. The alkaline earth metal halide catalysts showed broad reflexes which can be assigned to the respective alkaline earth chloride fluorides, MCIF. As already reported for dehydrochlorination reactions of hydrochlorofluorobutanes [18] the chloride fluoride phases are obviously the most stable ones under these reaction conditions.

#### 3.1.2. Surface area and porosity

The characteristic data of BET-surface area and porosity of the catalysts used here are summarized in Table 2. As can be seen, big differences between these catalysts exist, which however, do not correlate with the observed catalytic performances as will be demonstrated later.

**Table 2**

Characteristic topological data of the catalysts used.

Catalyst	Surface area	Porosity
F-Cr <sub>2</sub> O <sub>3</sub>	40 m <sup>2</sup> g <sup>-1</sup>	Mesoporous
HS-AlF <sub>3</sub>	200 m <sup>2</sup> g <sup>-1</sup>	Mesoporous
SrClF	40 m <sup>2</sup> g <sup>-1</sup>	Mesoporous
BaClF	60 m <sup>2</sup> g <sup>-1</sup>	Mesoporous

#### 3.1.3. Acid and base properties

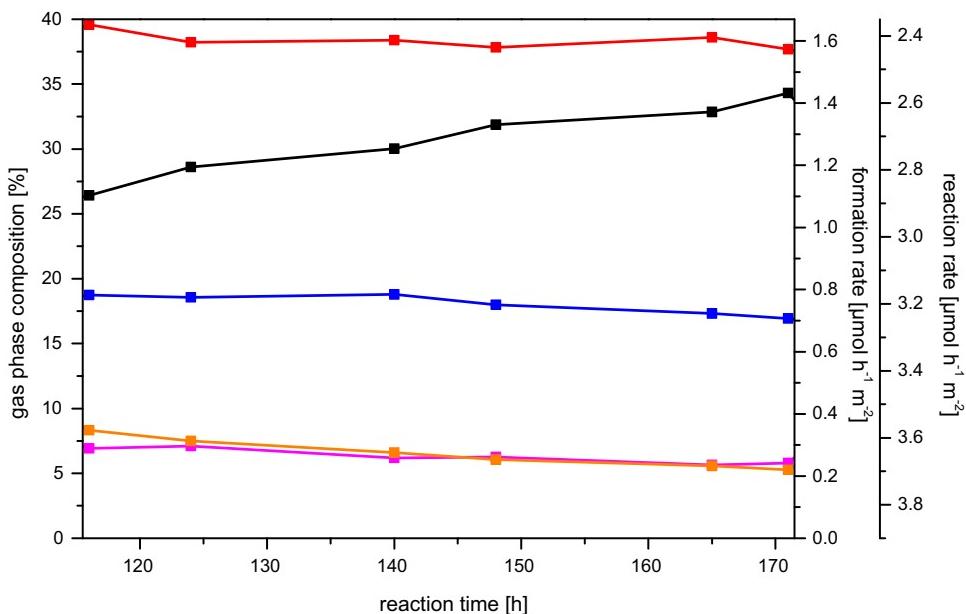
F-Cr<sub>2</sub>O<sub>3</sub> is known for its moderate Lewis acidity as stated in [20] but even Brønsted sites will be found when excess of HF is employed [11]. In line with this, the F-Cr<sub>2</sub>O<sub>3</sub> catalyst used here contains both Lewis and Brønsted acidic sites as well (FTIR spectroscopy with pyridine as probe molecule, see Fig. S2 in SI) due to the moderate calcination temperature used for Cr(OH)<sub>3</sub>. The NH<sub>3</sub>-TPD profiles for HS-AlF<sub>3</sub> and both chloride fluorides have already been comprehensively presented and discussed in [18]. HS-AlF<sub>3</sub> is known for its very strong Lewis acidic sites related to ammonia which desorbs above 400 °C [17]. The properties of both chloride fluorides obtained in this work were almost identical with those reported elsewhere thus indicating no or very weak acidic sites; this means desorption of ammonia was completed in all cases by 300 °C. In line with ammonia TPD results, comprehensive FTIR measurements of adsorbed CO indicate the presence of very weak Lewis acid sites only [18] whereas FTIR-investigations using CHCl<sub>3</sub> and pyrrole as probe molecules gave clear evidence for the presence of basic surface sites at these catalysts surfaces [18,21].

### 3.2. Catalytic results and mechanistic investigations

In the following, each possible reactant gas given in Scheme 1 was investigated in the heterogeneous reaction, under the conditions given in Table 1, in order to gain insight regarding the most probable reaction pathway from HCFO-1233xf to HFO-1234yf. Hence, besides HCFO-1233xf, HFO-1234yf, HFC-245cb and HCFC-244bb also were reacted in single steps and the gas phase distribution was followed. Different pressures, temperatures and contact times were applied in order to find out if coupled equilibria were present. Whereas the term “equilibrium” here refers to an equilibrated state related to performed reaction conditions obtained in the flow system as described in Section 2.2 and is not related to the thermodynamic equilibrium which relates to static conditions. Furthermore HS-AlF<sub>3</sub>, SrClF and BaClF were used as catalysts in some cases to gain additional information regarding possible dehydrochlorination reactions that might be involved too.

#### 3.2.1. Reaction of HCFO-1233xf with HF

The catalytic reactions of HCFO-1233xf with HF were started first with F-Cr<sub>2</sub>O<sub>3</sub> as catalyst and 20-fold excess of HF at 350 °C and 1 bar. Usually, chromia needs activation by fluorination which creates Lewis- acidic surface sites at which halogen exchange reaction can occur [22]. Since it is known that chromium surface sites in higher oxidation states than 3 in some fluorination reactions exhibit higher catalytic activity than Cr<sup>3+</sup>-surface sites [15], some oxygen was added to the gas phase reaction mixture to promote oxidation. After performing a common activation procedure as described



**Fig. 1.** Gas phase composition, reaction rate and formation rates for the reaction of HCFO-1233xf with HF at F-Cr<sub>2</sub>O<sub>3</sub>: black - HCFO-1233xf, red - HFO-1234yf, blue - HFC-245cb, magenta - other organics, orange - CO<sub>x</sub>; amount of HCFC-244bb is <0.1%.

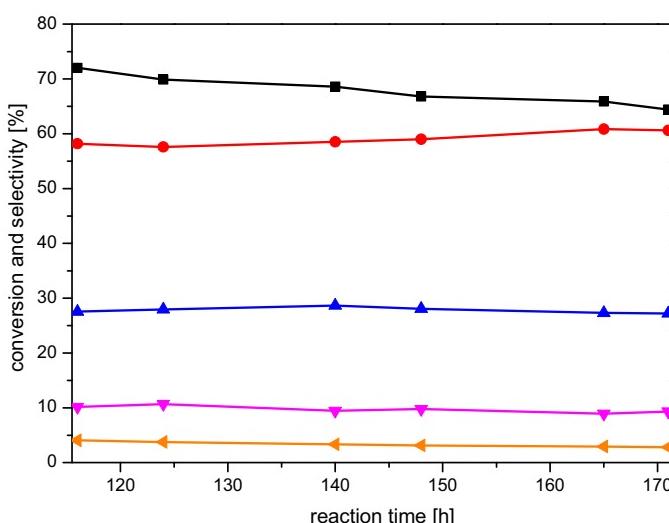
in [10,22 and references therein] an activity plateau at around 70% conversion (reaction rate  $\sim 2.8 \mu\text{mol h}^{-1}\text{m}^{-2}$ ) is observed (Figs. 1 and 2). It should be noted that addition of oxygen to the gas phase not only maintains a “certain degree” of oxidized chromium surface sites ( $\text{Cr}^{>3+}$ ) but at the same time also suppresses coke formation, thus leading to a significantly increased life time of the catalyst. As can be seen from Figs. 1 and 2 as well, HFO-1234yf is the main reaction product under these conditions whereas HCFC-244bb is only detected in traces quantities. Furthermore, formation of HFC-245cb is observed as the second most abundant reaction product. These two major products, on the first view, may argue for a reaction path HCFO-1233xf  $\rightarrow$  HFO-1234yf  $\rightarrow$  HFC-245cb. The formation of the later can be rationalized by a consecutive reaction of HFO-1234yf with HF according to Eq. 3. Besides formation of CO, CO<sub>2</sub> and other organic compounds (particularly isomers of HCFO-1233xf, HFO-1234yf and HFC-245cb some C-1 and C-2 compounds

like CH<sub>3</sub>Cl, CHF<sub>3</sub> and CF<sub>3</sub>-CH<sub>3</sub>) are observed in minor amounts which can be regarded as side reactions.

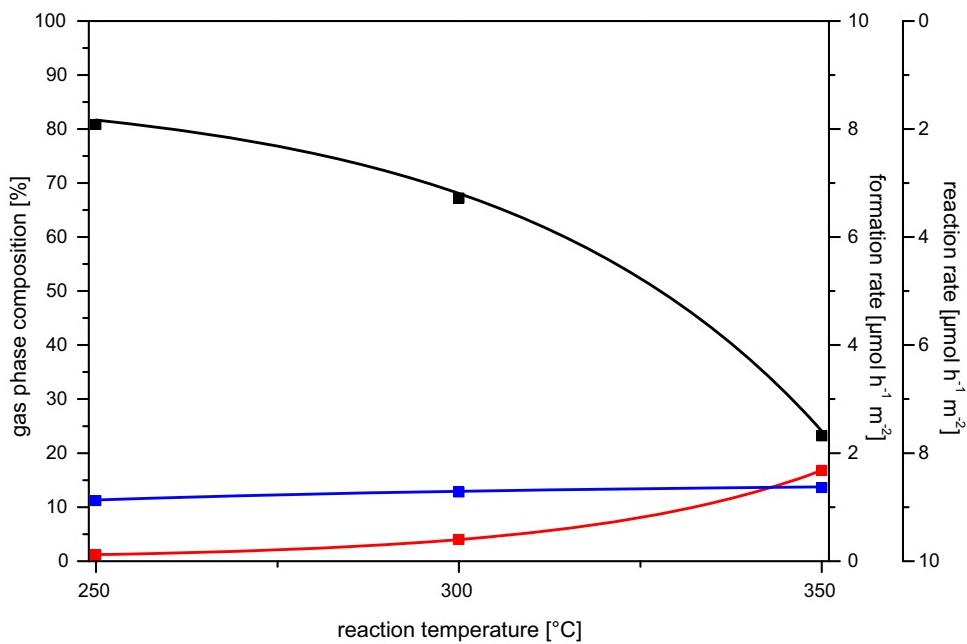
These results may indicate, that formation of HCFC-244bb can be ruled out. However, if this is just a very reactive intermediate directly formed from HCFO-1233xf (Eq. (2)) it might be consumed by fast consecutive reaction forming either HFO-1234yf (Eq. (4)) or/and HFC-245cb (Eq. (5)). In this case, running the reaction at lower temperature and lower HF gas phase concentration should display increased amounts of HCFC-244bb. Therefore, the reaction was repeated at lower temperatures and with only a 4-fold excess of HF (Fig. 3). Under these conditions too, HFO-1234yf and HFC-245cb were the only major products formed whereas no formation of HCFC-244bb was detected. This finding implies that the reaction between HCFO-1233xf with HF rather performs directly into the formation of HFO-1234yf (Eq. 1) but not via HCFC-244bb (Eq. 2). Surprisingly enough, although the conversion degree is not too high, HFC-245cb is formed to a higher degree than HFO-1234yf at and below 300 °C. Obviously, between 300 and 350 °C the equilibrium shifts drastically toward the formation of HFO-1234yf. This is a clear sign for a rapidly established and significant temperature dependent equilibrium between HFO-1234yf and HFC-245cb (Eq. (3)). It also is obvious that the reaction temperature should be at least 350 °C in order to ensure high degrees of conversion of HCFO-1233xf.

To prove the existence of an equilibrium between HFO-1234yf and HFC-245cb, the same reaction was performed at increased pressure (Table 3, column 4). The results indicate how easy the reaction equilibrium is determined by pressure changes: First, the conversion decreases as the total pressure increases and second, as expected, the equilibrium between HFO-1234yf and HFC-245cb significantly shifts toward the formation of the saturated hydrofluoroalkane HFC-245cb according the rule of LeChatelier. Under these conditions too, only traces of HCFC-244bb were found although formation of this saturated compound according to Eq. (2) should be favoured at increased pressure (rule of LeChatelier). This is a further argument against of HCFC-244bb formation as intermediate and for a direct conversion of HCFO-1233xf into HFO-1234yf (Eq. (1)).

Last but not least, contact time was varied between 0.1 and 10 s under a 10-fold excess of HF with special focus on the HFO-1234yf



**Fig. 2.** Conversion of HCFO-1233xf (black) and selectivity to HFO-1234yf (red), HFC-245cb (blue), other organics (magenta) and CO<sub>x</sub> (orange) for the reaction of HCFO-1233xf with HF at F-Cr<sub>2</sub>O<sub>3</sub>.



**Fig. 3.** Gas phase composition, reaction rate and formation rates for the reaction of HCFO-1233xf with HF at F-Cr<sub>2</sub>O<sub>3</sub> at different temperatures: black—HCFO-1233xf, red—HFO-1234yf, blue—HFC-245cb; HCFC-244bb was not evidenced.

**Table 3**  
Pressure dependence of the reaction of HCFO-1233xf with HF at F-Cr<sub>2</sub>O<sub>3</sub>: X – conversion in %, S – selectivity in %, R – reaction rate in  $\mu\text{mol h}^{-1} \text{m}^{-2}$ , F – formation rate in  $\mu\text{mol h}^{-1} \text{m}^{-2}$ .

Pressure	X <sub>HCFO-1233xf</sub>	S <sub>HFO-1234yf</sub>	S <sub>HFC-245cb</sub>	S <sub>HCFC-244bb</sub>	R <sub>HCFO-1233xf</sub>	F <sub>HFO-1234yf</sub>	F <sub>HFC-245cb</sub>	F <sub>HCFC-244bb</sub>
1 bar	69	59	29	≤ 0.1	2.7	1.6	0.8	0
3 bar	44	51	47	≤ 0.3	5.3	2.7	2.5	0
5 bar	35	38	59	≤ 0.7	6.9	2.6	4.1	0
7 bar	30	33	64	≤ 1.3	8.4	2.8	5.4	≤ 0.1

to HFC-245cb ratio (Fig. 4). Contact times longer than 5 s give constant HFO-1234yf to HFC-245cb ratios of 1.6: 1. If the contact time is shorter than 5 s the HFO-1234yf to HFC-245cb ratio increases strongly as the contact time decreases. At a contact time of 0.1 s a HFO-1234yf to HFC-245cb ratio of 5:1 was found. These results demonstrate a relatively rapidly (here: 5 s) established equilibrium

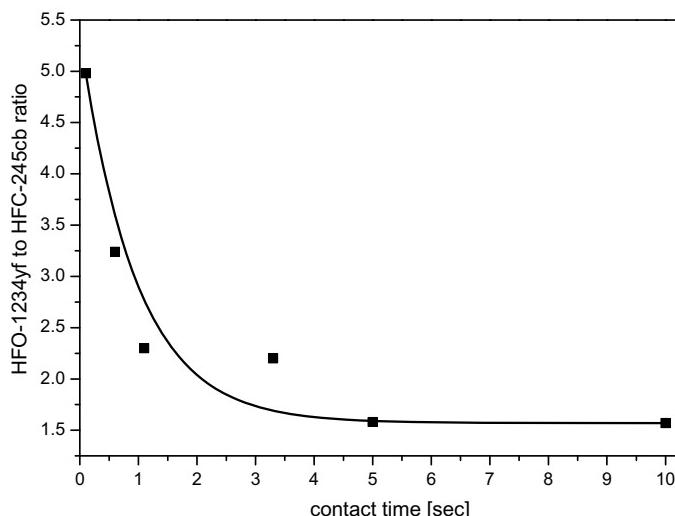
between these two compounds. At a contact time of 0.1 s a HFO-1234yf to HFC-245cb ratio of 5:1 was found, whereas already within 5 s a stable gas phase composition (HFO-1234yf: HFC-245cb ~1.7) is reached (Fig. 4). Furthermore, even at these very low contact times HCFC-244bb was not detected although it should be found if it really would be formed as intermediate.

These findings in combination with the high HFO-1234yf to HFC-245cb ratio at low contact time give strong evidence for a consecutive reaction of HCFO-1233xf with HF via direct chlorine for fluorine exchange leading to the formation of HFO-1234yf (Eq. (1)) followed by the formation of HFC-245cb via HF addition (Eq. (3)).

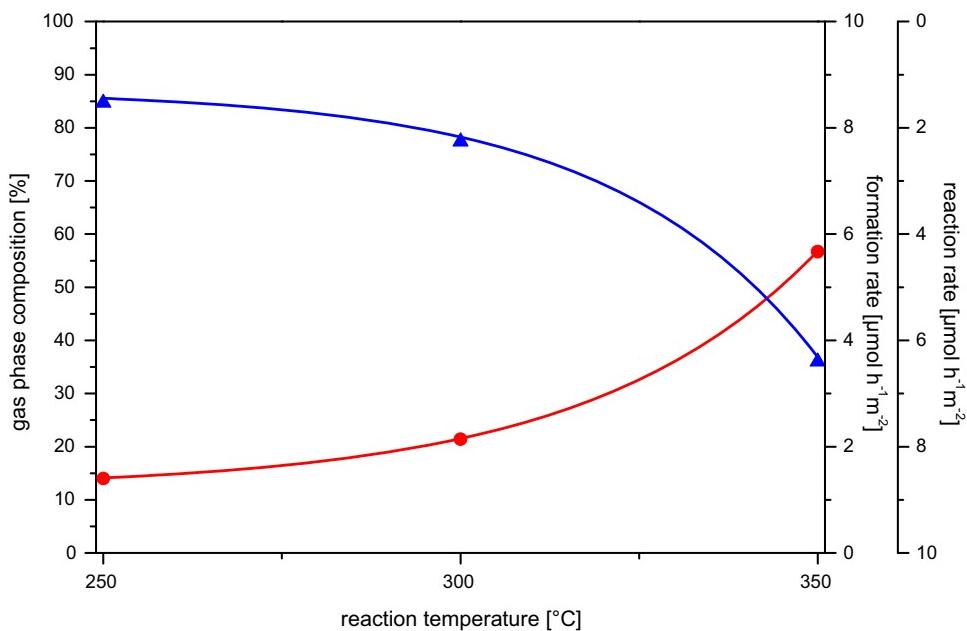
### 3.2.2. Reaction of HFO-1234yf with HF and HCl

The reaction for HFO-1234yf with HF corresponds to Eq. (3). The behaviour of HFO-1234yf at different temperatures over F-Cr<sub>2</sub>O<sub>3</sub> (Fig. 5) is in line with the former results. It should be noted that compared to the reaction of HCFO-1233xf with HF (according to Fig. 3) there is even 1 mol HF per mol HFO-1234yf more available to form HCFC-244bb because in the former case one mole HF becomes consumed for the formation of HFO-1234yf. However, almost the same relative distribution between HFO-1234yf and HCFC-245cb was found, again confirming a rapid establishment of the equilibrium (Eq. (3)).

The reaction between HFO-1234yf and HCl (Eq. 6 and Eq. 7) in the presence of F-Cr<sub>2</sub>O<sub>3</sub> was tested at 350 °C. Using a 1:1 mixture of HCl and HFO-1234yf, neither formation of HCFO-1233xf nor HCFC-244bb was observed. Increasing the HCl amount up to 40-fold excess, traces of HCFC-244bb were detected whereupon



**Fig. 4.** HFO-1234yf to HFC-245cb ratio at different contact times for the reaction of HCFO-1233xf with HF at F-Cr<sub>2</sub>O<sub>3</sub>.



**Fig. 5.** Gas phase composition, reaction rate and formation rates for the reaction of HFO-1234yf with HF at F-Cr<sub>2</sub>O<sub>3</sub> at different temperatures: red—HFO-1234yf, blue—HFC-245cb.

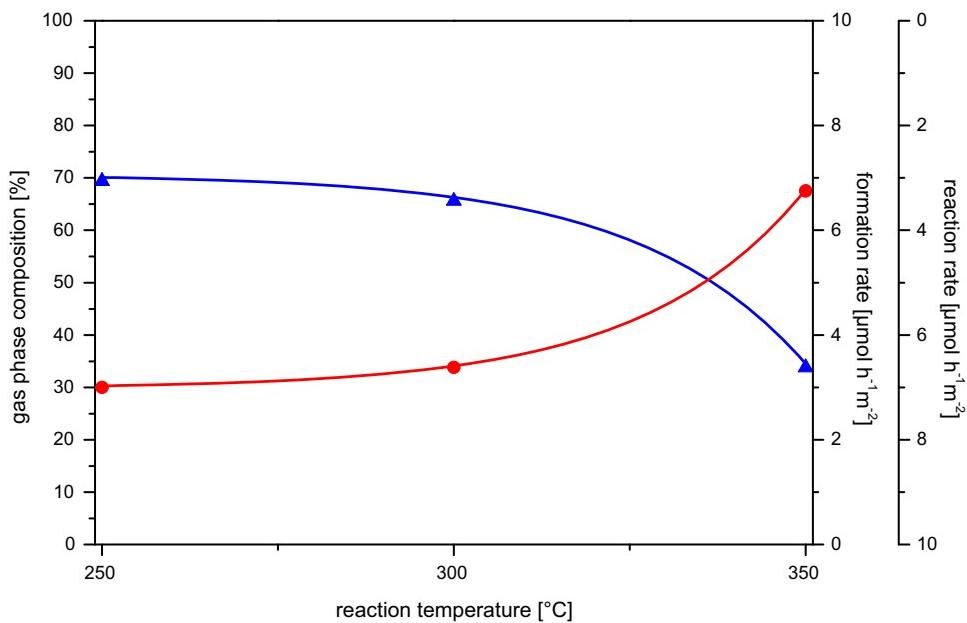
the amount of HCFO-1233xf was still <3% in the gas phase. This is a strong indication that once HFO-1234yf or HFC-245cb has been formed, there is no noticeable back reaction at all under the usual reaction conditions.

### 3.2.3. Behaviour of HFC-245cb

The behavior of HFC-245cb according to Eq. (8) is shown in Fig. 6. Interestingly enough, when starting from HFC-245cb without adding any HF, nearly the same distribution between HFO-1234yf and HFC-245cb was found as during previous experiments. This means, the reaction equilibrium between HCFC-245cb and HCFO-1234yf is very quickly established independent from which

direction the equilibrium is approached. The equilibrium composition shown in Fig. 6 was obtained without adding HF to HFC-245cb, but almost the same equilibrium composition was obtained even when 1 mol HF was added per 1 mol HFC-245cb, indicating that the HF partial pressure has only limited impact, and suggesting that the temperature has a significantly higher impact on the equilibrium.

As a matter of fact, all of the reaction systems HCFO-1233xf, HFO-1234yf and HFC-245cb demonstrate a strong temperature dependence of the HFO-1234yf to HFC-245cb equilibrium observed in all these three partial reactions whereas this equilibrium seems almost independent of the partial pressure of HF providing the



**Fig. 6.** Gas phase composition, reaction rate and formation rates for the reaction of HFC-245cb at F-Cr<sub>2</sub>O<sub>3</sub> at different temperatures: red—HFO-1234yf, blue—HFC-245cb.

**Table 4**

Reaction of HCFC-244bb (with HF) at different catalysts: X – conversion in %, S – selectivity in %, R – reaction rate in  $\mu\text{mol h}^{-1} \text{m}^{-2}$ , F – formation rate in  $\mu\text{mol h}^{-1} \text{m}^{-2}$ .

Catalyst	$X_{\text{HCFC-244bb}}$	$S_{\text{HCFO-1233xf}}$	$S_{\text{HFO-1234yf}}$	$S_{\text{HFC-245cb}}$	$R_{\text{HCFC-244bb}}$	$F_{\text{HCFO-1233xf}}$	$F_{\text{HFO-1234yf}}$	$F_{\text{HFC-245cb}}$
Without	0.7	81	12	3	–	–	–	–
$\text{F-Cr}_2\text{O}_3$	100	50	29	20	15.5	7.7	4.5	3.1
$\text{HS-AlF}_3$	100	99	0.1	0.1	7.8	7.7	0	0
$\text{SrClF}$	55	4	96	0.1	4.3	0.2	4.1	0
$\text{BaClF}$	54	5	95	0.1	4.1	0.2	3.9	0

overall pressure does not change. According to LeChatelier's principle, the equilibrium shifts to the saturated HFC-245cb by increasing the overall pressure.

### 3.2.4. Behaviour of HCFC-244bb

In order to definitely rule out the formation of HCFC-244bb as intermediate, the reaction behaviour of the former was investigated by performing all possible reactions by using it as reactant and following the product compositions. In principle, HCFC-244bb can either undergo chlorine/fluorine exchange forming HFC-245cb (Eq. (4)) or/and dehydrochlorination forming HFO-1234yf (Eq. (5)) which might further react forming HFC-245cb as consecutive product (Eq. (3)), or may undergo dehydrofluorination reaction forming HCFO-1233xf (Eq. (9)). Owing to the limited availability of HCFC-244bb, only reactions at 350 °C as the most promising reaction temperature of HFO-1234yf formation were investigated and these results are summarized in Table 4.

Without any catalyst (row 1) less than 1% conversion was found thus demonstrating the thermal stability of HCFC-244bb. The situation is quite different if  $\text{F-Cr}_2\text{O}_3$  as catalyst is involved (row 2): 100% conversion of HCFC-244bb is obtained whereupon the major product is HCFO-1233xf. Although formed to a minor content, the equilibrium distribution between the fluorinated products HFO-1234yf and HFC-245cb does not change as compared to that when HCFO-1233xf is used as starting reactant. Obviously, dehydrofluorination of HCFC-244bb resulting in HCFO-1233xf formation (Eq. (9)) is the dominant reaction, more than ever because the back reaction according to Eq. (6) can be excluded. Based on these findings, formation of HCFC-244bb from HCFO-1233xf (Eq. (2)) has to be ruled out under these reaction conditions.

Under homogeneously catalysed reaction conditions formation of HCFC-244bb as stable intermediate compound is the dominant reaction step as disclosed in [9]. In contrast, under heterogeneous conditions with the  $\text{F-Cr}_2\text{O}_3$ -catalyst an almost complete conversion of HCFC-244bb with HCFO-1233xf as the major product has been evidenced. This means, the reaction channel under heterogeneous reaction conditions is distinctly different to that observed for homogenous conditions with an antimony pentafluoride based catalyst. Since HCFC-244bb in presence of an  $\text{F-Cr}_2\text{O}_3$  catalyst evidently undergoes fast dehydrofluorination (Eq. (9)) thus forming HCFO-1233xf, its formation under these conditions can be excluded. Moreover, the product distribution towards HFO-1234yf and HFC-245cb corresponds very well with the results presented previously thus suggesting that both these products were formed from HCFO-1233xf as preliminary dehydrofluorination product of HCFC-244bb. Consequently we checked the reported excellent dehydrofluorination catalyst  $\text{HS-AlF}_3$  [18] which is an even stronger Lewis acid than  $\text{F-Cr}_2\text{O}_3$ . As can be seen from the data in Table 4 (row 3), almost complete conversion into HCFO-1233xf as the sole product was observed. It was found in separate tests that  $\text{HS-AlF}_3$  is too Lewis acidic to catalyze the conversion of HCFO-1233xf into HFO-1234yf due to blocked surface sites as a result of too strong adsorption of HF. Compounds  $\text{SrClF}$  and  $\text{BaClF}$  (Table 4, rows 4 and 5) were also evaluated as they have, in past studies, been found to be excellent dehydrochlorination catalysts for fluorochlorobutanes [18]. As expected, reasonably good conversion with extremely high

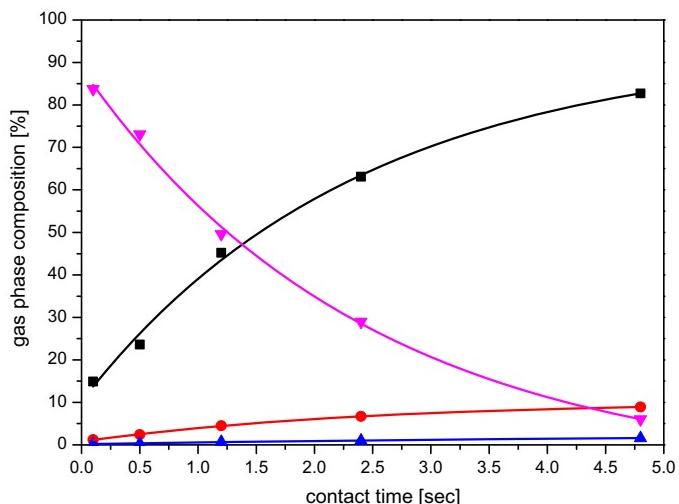


Fig. 7. Gas phase composition for the reaction of HCFC-244bb at  $\text{F-Cr}_2\text{O}_3$  at different contact times: black—HCFO-1233xf, red—HFO-1234yf, blue—HFC-245cb, magenta — HCFC-244bb.

selectivity toward the dehydrochlorination product HFO-1234yf was obtained. It is important to note that no conversion at all was observed when barium fluoride catalyst was used for the reaction of HCFO-1233xf with HF.

In order to further support the deduced reaction path, the behavior of HCFC-244bb without any HF addition in the presence of the  $\text{F-Cr}_2\text{O}_3$  catalyst at 350 °C was investigated as a function of the contact time (Fig. 7 and Table 5). As expected, by shortening the contact time, conversion of HFO-244bb decreased. The compound which forms directly from HCFC-244bb should be the major reaction product observed, and especially at low contact times. This is found to be HCFO-1233xf formed according to Eq. (9). Formation of HFO-1234yf and HFC-245cb is observed as well. Hence, availability of HF is limited to dehydrofluorination of HCFC-244bb, resulting in the formation of HCFO-1233xf, hydrofluorination of the latter strongly depends on conversion of HCFC-244bb. Therefore, it is not surprising that the selectivities towards HCFO-1233xf, HFO-1234yf and HFC-245cb are largely independent of contact time.

As a matter of fact these results demonstrate that under typical reaction conditions, HCFC-244bb is selectively converted to HCFO-1233xf (Eq. (9)). This precludes the formation of HCFC-244bb by hydrofluorination according to Eq. (2) when reacting HCFO-1233xf with HF, and supports the reaction path according to Eq. (1) via chlorine for fluorine exchange leading directly to HFO-1234yf.

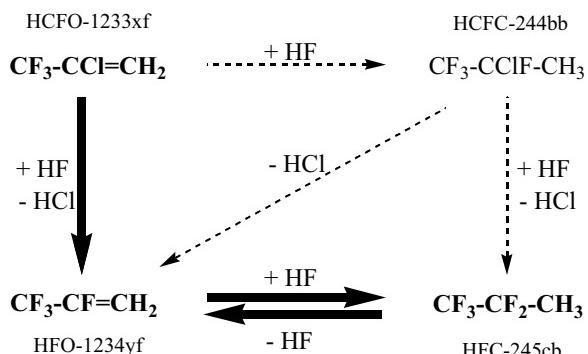
## 4. Discussion: The reaction path

As outlined in the introduction, it was not the intention of this paper to investigate in detail the parameters for an optimized chromia based catalyst. However, in line with reports in literature and a recently published paper on this reaction [10] we also found that coke formation is an issue for catalyst deactivation. Hence, we run all the reactions in presence of oxygen thus enhancing the life time of the catalysts employed. Under the conditions used here we found

**Table 5**

Reaction of HCFC-244bb at F-Cr<sub>2</sub>O<sub>3</sub> at different contact times: X – conversion in %, S – selectivity in %, R – reaction rate in  $\mu\text{mol h}^{-1}\text{m}^{-2}$ , F – formation rate in  $\mu\text{mol h}^{-1}\text{m}^{-2}$ .

Contact time	X <sub>HCFC-244bb</sub>	S <sub>HCFO-1233xf</sub>	S <sub>HFO-1234yf</sub>	S <sub>HFC-245cb</sub>	R <sub>HCFC-244bb</sub>	F <sub>HCFO-1233xf</sub>	F <sub>HFO-1234yf</sub>	F <sub>HFC-245cb</sub>
0.1 s	16	91	7.4	1.2	408	373	30	5
0.5 s	27	88	8.9	1.1	168	148	15	2
1.2 s	50	90	8.9	1.4	126	113	11	2
2.4 s	71	89	9.4	1.4	89	79	8	1
4.8 s	94	88	9.4	1.7	59	52	6	1



**Scheme 2.** Most probable reaction pathways (bold) for the reaction of HCFO-1233xf with HF at F-Cr<sub>2</sub>O<sub>3</sub>.

less impact of the possible Deacon reaction (formation of chlorine gas) which was almost in the range of 1 to 1.5% as deduced from the content of over halogenated impurities from the reaction with chlorine.

By comparing the product distributions obtained from the separate reactions of all the possible fluorocarbon intermediates with HF a reaction path directly from HCFO-1233xf to HFO-1234yf that immediately establishes a very temperature sensitive equilibrium with HFC-245cb is evident (cf. bold reaction paths in Scheme 2).

As opposed to liquid phase catalyzed reactions [12], no experimental evidence for the intermediate formation of HCFC-244bb was obtained. Thus, in the presence of F-Cr<sub>2</sub>O<sub>3</sub> catalyst almost the same distribution between HCFO-1233xf, HFO-1234yf and HFC-245cb was found starting from either HCFC-244bb or HCFO-1233xf and HF. Please keep in mind there is almost no HCFO-1233xf formation when starting from HFO-1234yf and equimolar amounts of HCl, meaning this reaction channel does not exist under heterogeneous conditions. Most importantly to notice is that HCFO-1233xf was always the major compound when starting with HCFC-244bb as reactant in presence of F-Cr<sub>2</sub>O<sub>3</sub>. The conclusion is obvious: starting from HCFC-244bb in presence of F-Cr<sub>2</sub>O<sub>3</sub> results dominantly in the formation of 1233xf but not HFO-1234yf. Only in presence of strong dehydrochlorination catalysts like BaF<sub>2</sub> or SrF<sub>2</sub>, respectively, direct formation of HFO-1234yf from HCFC-244bb was observed. In contrast, solid Lewis acids like F-Cr<sub>2</sub>O<sub>3</sub> selectively catalyze dehydrofluorination, thus forming HCFO-1233xf when starting with HCFC-244bb as reactant.

This presents a strong argument against the intermediate formation of HCFC-244bb in the case of the heterogeneous gas phase fluorination of HCFO-1233xf since HCFC-244bb in the presence of F-Cr<sub>2</sub>O<sub>3</sub> catalyst at 350 °C immediately undergoes complete conversion into HCFO-1233xf as the major product and just small amounts of HFO-1234yf and HFC-245cb were found. Thus, the formation of large amounts of HCFO-1233xf from HCFC-244bb as starting reactant molecule is a strong argument against a reaction sequence HCFC-244bb → HFO-1234yf → HCFO-1233xf, especially because the reaction of HFO-1234yf with excess HCl gave only negligible traces of HCFO-1233xf.

The conclusion therefore is formation of HCFC-244bb according to Eq. (2) as an intermediate in the reaction of HCFO-1233xf

with HF can be excluded under heterogeneous gas phase conditions since our results evidently show that it is not at all stable under these conditions in the presence of a solid catalyst but immediately extrudes HF with formation of HCFO-1233xf. Hence, there is no evidence for its formation in detectable amounts. There is not final explanation for this evident difference between homogeneous and heterogeneous catalytic conditions, however, since our investigations clearly have shown a drastic impact of the reaction temperature on all the equilibria involved here, it might be speculated that the temperature might be the most decisive factor.

Moreover, the even stronger solid Lewis acid HS-AlF<sub>3</sub>, known as an excellent dehydrofluorination catalyst, selectively converted HCFC-244bb into HCFO-1233xf, however, practically no HFO-1234yf was formed and consequently, neither HFC-245cb was found. This even more strongly supports the conclusion that direct transformation of HCFC-244bb into HFC-245cb by chlorine against fluorine exchange (cf. also Eq. (4)) under heterogeneous catalytic conditions does not at all occur on Lewis acidic sites. We also checked the reaction of HCFO-1233xf with HF in presence of HS-AlF<sub>3</sub> as catalyst and, in line with the above reported results, did not find remarkable conversion into HFO-1234yf probably due to blocking of the Lewis acidic surface sites by HF. On the other hand, with the well-known dehydrochlorination catalysts SrClF and BaClF, at ca. 55% HCFC-244bb conversion nearly exclusive formation of HFO-1234yf was found, but no HFC-245cb and just small amounts of HCFO-1233xf (cf. Table 4). This can be rationalized based on the fact that BaClF does not exhibit any detectable Lewis acid surface sites [18].

Last but not least, using DF instead of HF for gaining more mechanistic insights is not applicable in this reaction system since on the one hand dehydrochlorination and dedeuteriochlorination will very likely occur simultaneously, and on the other hand, even more importantly, HF/DF and HCl/DCI in presence of a solid Lewis acid very easily undergo isotope exchange reactions [23] (see SI for more details).

## 5. Conclusion

In conclusion, on fluorinated chromia as an excellent solid catalyst for this type of Lewis acid catalyzed gas phase reactions a direct conversion of HCFO-1233xf via chlorine for fluorine exchange reaction into the desired product HFO-1234yf was demonstrated. In opposition to the well documented formation of HFC-244bb as intermediate during the conversion of HCFO-1233xf by HF into HFO-1234yf in homogeneous liquid phase conditions, its formation can be evidently excluded under heterogeneous gas phase conditions at temperatures above 250 °C. Although HFO-1234yf very quickly establishes an equilibrium with HFC-245cb, the selectivity towards the desired olefin can be drastically shifted simply by adjusting the temperature applied during reaction: The higher the temperature the more this equilibrium is shifted towards HFO-1234yf. Applying higher pressures is counter-productive since this shifts the equilibrium toward the undesired saturated HFC-245cb.

Another interesting point is the behavior of HCFC-244bb as one of the major intermediate compounds formed under homogenous liquid phase conditions with catalysts that support

dehydrochlorination reactions, e.g. BaClF or SrClF. These catalysts selectively convert HCFC-244bb by dehydrochlorination with ~95% selectivity into HFO-1234yf, thus opening the opportunity of using HCFC-244bb as feedstock for the very convenient and highly selective formation of HFO-1234yf under heterogeneous gas phase conditions.

Although not extensively reflected here, addition of certain amounts of oxygen to the reactant gas mixture increases both the conversion of HCFO-1233xf and the lifetime of the catalysts. The role of oxygen and its impact on the formation of catalytically active surface sites is a topic of ongoing investigations.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2014.09.076>.

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